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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method of Preparing ε-Caprolactone and Derivatives thereof Free of Explosive Peroxides

We, CHISSO CORPORATION, of No. 1 Sozecho Kitaku Osaka, Japan, a Japanese body corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described, in and by the following statement:—

The present invention relates to a method of preparing ε-caprolactone and derivatives thereof, such as oligomers and polyesters, free of explosive peroxides. Specifically, the invention consists broadly in a process in which derivatives of ε-caprolactone containing explosive peroxides are treated with an aqueous acid solution containing at least 1 gram ion of cuprous or ferrous ions for each mole of peroxide linkage, so as to hydrolyse the said peroxides. The term "derivatives of ε-caprolactone" is here defined to mean linear and/or cyclic oligomeric esters and/or linear higher polyesters from the bifunctional esterification of ε-hydroxy-caproic acid. The derivatives moreover, may also contain ε-caprolactone itself and/or ε-hydroxy-caproic acid.

Preferably the said derivatives of ε-caprolactone are obtained by the oxidation of cyclohexanone or cyclohexanol with hydrogen peroxide, oxygen or an oxygen-containing gas. The resulting oxidation products may then be treated under acid conditions with, for example, an organic or inorganic mineral acid or anhydride.

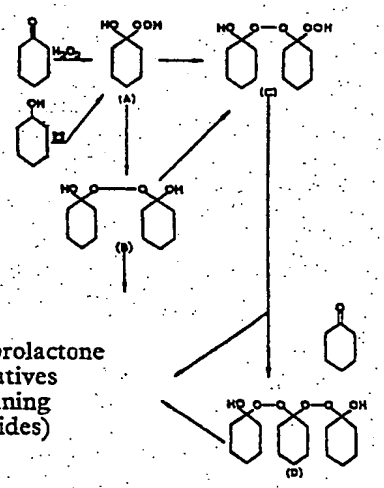
The method of preparing ε-caprolactone and derivatives thereof by the oxidation of cyclohexanone or cyclohexanol is well known. For example, in Japanese Patent Publications Nos. 735/66 and 736/66 there are described methods for treating hydroperoxides, which are the oxidation products derived from the reaction of cyclohexanol with hydrogen peroxide, with inorganic or organic acids to obtain ε-caprolactone or derivatives thereof.

[*Price 5s. 0d.*]

However, these methods of producing the derivatives of ε-caprolactone also produce large quantities of explosive peroxides and it is therefore extremely dangerous to attempt to isolate ε-caprolactone from the reaction product by heating or by reacting the derivatives with aqueous ammonia to form ε-caprolactam, as high temperatures are required.

It has been found that ε-caprolactone and derivatives thereof together with explosive peroxides are formed in the following cases.

The reaction scheme in some cases is shown as follows:



(ε-caprolactone derivatives containing peroxides)

(a) The hydroperoxide obtained by the reaction of equimolar amounts of cyclohexanone and aqueous hydrogen peroxide in the presence of a mineral acid catalyst at room temperature or an elevated temperature was 1 - hydroxy - 1′ - hydroperoxy dicyclohexyl peroxide (C) which was formed directly from 1 - hydroxy - 1 - hydroperoxy cyclohexane (A) or by way of 1, 1′ - dihydroxy - dicyclo - hexyl peroxide (B).

The treatment of one mole of hydroperoxide (C) with an organic or inorganic acid, such as acetic acid, preferably at an elevated temperature, gave about one mole of cyclohexanone and less than one mole of ε-caprolactone derivatives.

(b) The hydroperoxide (C) was reacted with equimolar amounts of cyclohexanone to form a mixture containing peroxide (D), which, on heating in the presence of an acid, gave one mole of cyclohexanone and less than two moles of ε-caprolactone derivatives.

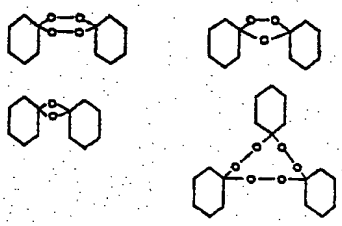
(c) The hydroperoxide (A) obtained from the oxidation of cyclohexanol by oxygen in the presence of a radical initiator such as a peroxide, was treated with an inorganic or organic acid or acetic anhydride at an elevated temperature to give mainly ε-caprolactone derivatives.

(d) The treatment of a mixture containing mainly peroxide (B) obtained from one mole of hydroperoxide (A) and an equimolar amount of cyclohexanone in accordance with the above-mentioned method (c) gave one mole of cyclohexanone and less than one mole of ε-caprolactone derivatives.

(e) When cyclohexanone was oxidized with aqueous hydrogen peroxide under alkaline conditions, an oily or solid product containing mainly ε-caprolactone derivatives was obtained.

The oily or solid products comprising ε-caprolactone derivatives obtained in the above-mentioned cases contained considerable amounts of peroxides, in some cases more than several percent thereof, which would not oxidize potassium iodide at room temperature and could not be easily decomposed by a reducing agent such as sodium hydrogen sulfite, especially in the presence of oxygen and under alkaline conditions at room temperature.

Examples of the explosive peroxides present in the derivatives of ε-caprolactone so prepared are believed to be:



ε-caprolactone derivatives containing such peroxides are liable to explode, depending upon the amount of explosive peroxides.

Cuprous ions and ferrous ions can be used not only in the form of an inorganic acid salt but also in any other form which will produce the metal ions. However the sulphate and chloride are especially preferable.

The chloride is particularly preferred because of its high solubility.

When an aqueous hydrochloric acid solution containing cuprous chloride is used, a further addition of a salt such as sodium chloride or potassium chloride gives an improved result because of the increased solubility of cuprous chloride.

The addition of substances to increase the solubility of the cuprous or ferrous ions in the treating solution of this invention is preferable and accordingly is included in the scope of the present invention.

Acids applicable in the present invention have no particular limitation unless any sparingly soluble salt is formed in the process of the invention. Exemplary acids are inorganic acids such as hydrochloric acid, sulfuric acid or sulfurous acid and organic acids such as acetic acid.

The amounts of the cuprous or ferrous ions to be included in the aqueous acid solution are preferably more than equimolar amounts relative to the peroxides contained in ε-caprolactone derivatives.

The concentration of the metallic ion in the aqueous acid solution has no particular limitation.

The acidity of the aqueous solution may be of any pH which is sufficient for hydrolysis of peroxides to hydroperoxides, generally a pH less than 2, preferably less than 1, is used.

In the treatment of ε-caprolactone derivatives with the above-mentioned aqueous acid solution in the present method, they may be simply mixed with the solution and allowed to stand.

The reaction temperature has no particular limitation. The complete decomposition of the peroxides occurs in eight hours at room temperature, but a suitably elevated temperature promotes the hydrolysis of peroxides and the decomposition is complete within several minutes.

When the reaction is performed with heating, the temperature is preferably between 40° C—80° C to avoid boiling the water.

According to the method of the present invention, peroxides are hydrolysed to hydroperoxides, which decompose rapidly to form a stable compound. Thus the danger of explosion is completely absent in the present method.

ε-Caprolactone derivatives thus obtained can be safely heated in the presence of sodium hydroxide at an elevated temperature of about 210°—320° C followed by distillation at reduced pressure to recover ε-caprolactone. Also, the reaction with ammonia water at a high temperature can yield safely ε-caprolactam.

The invention will be further described by the following Examples.

EXAMPLE 1.

50 g of cyclohexanone and 110 g of 30% aqueous hydrogen peroxide were added dropwise with stirring at 50—55° C to carry out the oxidation. After the addition, the solution was kept at this temperature for four hours.

After cooling the reaction mixture, it was extracted with ether and 5.5 g of unreacted cyclohexanone were recovered.

The water layer was then neutralized with hydrochloric acid and was added to a solution comprising 5 g of cuprous chloride, 20 g of sodium chloride and some quantities of 6N aqueous hydrochloric acid.

The mixture was allowed to stand for an hour and complete decomposition of the peroxides took place.

The resultant oily product was extracted with ether, washed with water and concentrated. After removing the solvent, 0.5 g of sodium hydroxide was added and the mixture was introduced into a distillation apparatus. After heating for three hours at 280° C on an oil bath, the product was distilled *in vacuo* at 20 mm Hg and at further reduced pressure. 41 g of ε-caprolactone having a boiling point of 78—82° C/3mm Hg were safely obtained (yield 70.6%).

EXAMPLE 2.

When 49 g of cyclohexanone and 57 g of aqueous hydrogen peroxide (30%) were mixed in the presence of 1 ml. of conc. hydrochloric acid, the mixture became slightly warm. After allowing the mixture to stand for six hours followed by cooling 63.5 g of crystalline hydroperoxide were obtained (yield 96%, m.p. 65—82° C). 49.2 g of this solid were dissolved in 46 g of acetic anhydride and 200 cc. of benzene were added. The mixture was refluxed for eight hours on water bath. It was then introduced into a solution comprising 5 g of cuprous chloride, 10 g of sodium chloride and 100 cc of 2N hydrochloric acid.

After standing over night, the mixture was heated for two hours and separated into organic and water layers, and the latter was extracted with ether. The combined ether extract and organic layer was concentrated by evaporation with heating.

A part of the combined liquid was heated with potassium iodide containing hydrochloric acid, but it did not liberate iodine.

After the concentration of the solution, 0.5 g of sodium hydroxide was added to the concentrate and the mixture was introduced into a distillation apparatus.

Heating for three hours at 260—330° C followed by distillation *in vacuo* at 20 mm Hg gave safely 18.0 g of cyclohexanone and 18.4 g of ε-caprolactone.

According to the assumption that one mole of hydroperoxide gives one mole of cyclohexanone and one mole of ε-caprolactone, the yields are 92% and 80.5%, respectively.

Hydrolytic decomposition of peroxide-containing liquid (from the treatment of the hydroperoxide with acetic anhydride and benzene) obtained in the same way as in Example 2 was carried out using ferrous ions. The peroxide-containing liquid was added to a mixture of 5 g of ferrous sulfate and 100 cc of 2N sulfuric acid. After standing, the mixture was heated for 2 hours. In the KI test thereto, iodine was not liberated. The same separation, concentration and distillation steps as in Example 2 were carried out. The distillate was safely obtained. Yield of ε-caprolactone was 75%. When an aqueous neutral solution of ferrous sulfate was used, complete decomposition of the peroxide was not observed at room temperature, even after standing of seven days.

EXAMPLE 3.

24.6 g of the hydroperoxide obtained from Example 2, 9.8 g of cyclohexanone and three drops of conc. hydrochloric acid were mixed and warmed until the solid dissolved and then allowed to stand all night, which gave colourless crystals again. 18.9 g of these crystals, 12 g of acetic anhydride and 50 cc of benzene were mixed and refluxed for 10 hours on a water bath. The reaction product was added to a solution comprising 5g of cuprous chloride, 10 g of sodium chloride and 100 cc of 2N hydrochloric acid, and the mixture was allowed to stand all night and then refluxed for 2 hours. A part of the solution was warmed in a solution of potassium iodide containing hydrochloric acid but did not liberate iodine. After the separation of the organic layer and water layer, the former was washed with water to remove copper ions and the latter was extracted with ether and the extract was washed by water. The combined ether extract and organic liquid was concentrated. 0.2 g of sodium hydroxide was added to the concentrated liquid, which mixture was heated to 260° to 320° C and distilled *in vacuo* at 20 mm Hg until the distillation ceased. As a result 5.0 g. of cyclohexanone and 8.2 g of ε-caprolactone were safetly obtained.

According to the assumption that one mole of hydroperoxide gives one mole of cyclohexanone and two moles of ε-caprolactone, the yields were 93% and 66%, respectively.

EXAMPLE 4

ε-Caprolactone derivatives containing peroxides were obtained under the same conditions as in Example 3. The reaction product was added to a solution consisting of 1 g of cuprous chloride, 1 g of sodium chloride, 5 g of sodium hydrogen sulfite and 100 cc of 2N hydrochloride acid. After standing over

night, the solution did not liberate any more iodine. Using only sodium hydrogen sulfite to decompose the peroxides (i.e. without any cuprous chloride) decomposition occurred to a small extent but was not complete even when the reaction mixture was left over night. The product was then treated as in Example 3, 8.0 g of caprolactone were safely obtained.

EXAMPLE 5.

240 g of cyclohexanol and 1.01 g of methyl ethyl ketone peroxide were introduced into three-necked flask and heated to 98° C in the presence of oxygen. The mixture was oxidised with stirring by the slow addition of molecular oxygen.

The products were removed after 16 hours and a quantitative estimation of hydroperoxides showed 0.216 mole of hydroperoxides e.g. 1 - hydroxy - 1' - hydroperoxy - cyclo - hexane. After 0.19 mole of the peroxide and 24 g of acetic acid were mixed and warmed at 80° C for 40 hours, the product was introduced into the solution containing 5 g of cuprous chloride, 10 g of sodium chloride and 100 cc of 2N hydrochloric acid and heated at 80° C for 2 hours.

The organic layer was separated, and the water layer was extracted with ether.

0.2 g of sodium hydroxide was added into the combined organic layer and ether extract, and the mixture was introduced into the distillation flask. After water, acetic acid and cyclohexanol were removed at atmospheric pressure, the whole was heated to between 260° C and 320° C and then distilled at 20 mm Hg until the distillation ceased. 0.09 mole of ε-caprolactone (10.3 g) was safely obtained (yield 42.5%).

A product was prepared as above by the reaction of a solution containing 1, 1'- di - hydroxy - dicyclohexyl peroxide and 18.5 g of cyclohexanone. This product was treated as above to give ε-caprolactone in good yield safely (74%).

WHAT WE CLAIM IS:—

1. A process in which derivatives of ε-caprolactone (as hereinbefore defined) containing explosive peroxides are treated with an aqueous acid solution containing at least 1 gm of cuprous or ferrous ions for each mole of peroxide linkage so as to hydrolyse the said peroxides.

2. A process according to claim 1, in which said derivatives also contain ε-caprolactone and/or ε-hydroxy-caproic acid.

3. A process according to any preceding claim, in which the said derivatives are obtained by a method which comprises the oxidation of cyclohexanone or cyclohexanol with hydrogen peroxide, oxygen or an oxygen-containing gas.

4. A process according to claim 3 in which the products of oxidation of cyclohexanone or cyclohexanol are additionally treated with an organic or inorganic mineral acid.

5. A process according to any one of claims 1 to 4, in which the said cuprous ions are obtained from cuprous chloride.

6. A method according to any one of claims 1 to 4, in which said ferrous ions are obtained from ferrous sulphate.

7. A process according to any preceding claim, in which, after said explosive peroxides have been hydrolysed, said derivatives of ε-caprolactone are distilled to produce ε-caprolactone.

8. A process according to claim 1, substantially as hereinbefore described with reference to any of the foregoing Examples.

9. A process according to claim 7, substantially as hereinbefore described with reference to any of the foregoing Examples.

10. Derivatives of ε-caprolactone when treated by the process of any one of claims 1 to 6 or 8.

11. ε-Caprolactone when prepared by the process of claim 7 or claim 9.

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